

The fragment bis(acetylacetonato)ruthenium: a meeting-point of coordination and organometallic chemistry

Martin A. Bennett^{*}, Matthew J. Byrnes, Ivan Kováčik

Research School of Chemistry, Australian National University, Science Road, Canberra ACT 0200, Australia

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Abstract

Reduction of $[\text{Ru}(\text{acac})_3]$ with zinc in THF/ H_2O provides a range of coordination and organometallic complexes containing $\text{Ru}^{\text{II}}(\text{acac})_2$, whose chemistry is reviewed. Most of these compounds, including those containing alkenes, undergo reversible one-electron oxidation to their $\text{Ru}^{\text{III}}(\text{acac})_2$ counterparts, and the alkene–ruthenium(III) cations have been detected by spectroelectrochemistry. The cations derived from the chelate N-donor ligands *o*- $\text{CH}_2=\text{CHC}_6\text{H}_4\text{NMe}_2$ and *o*- $\text{PhC}\equiv\text{CC}_6\text{H}_4\text{NMe}_2$ have been isolated and structurally characterized. Comparison of the metrical data establishes that, whereas the alkene is less firmly bound to Ru^{III} than to Ru^{II} , the alkyne is bound about as strongly to Ru^{III} as to Ru^{II} . Some uncharged nucleophiles (pyridine, diethylamine, PPh_3) react with the cationic Ru^{III} complexes to give unusual, paramagnetic $\text{Ru}^{\text{III}}\text{–C}$ σ -bonded chelate complexes.
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1. Background

Among mononuclear dipositive d-block metal ions, ruthenium(II) and, to an even greater extent, osmium(II) are notable for the ability of their classical coordination complexes containing typical ‘hard’ ligands such as H_2O and NH_3 to bind ‘soft’ π -acceptor ligands such as CO, N_2 , alkenes, alkynes and tertiary phosphines [1]. For example, for ruthenium(II), this property is manifest in the existence of stable, cationic alkene complexes, such as $[\text{Ru}(\text{NH}_3)_5(\eta^2\text{-C}_2\text{H}_4)]^{2+}$ [2], $[\text{Ru}(\text{NH}_3)_4(s\text{-trans-}\eta^4\text{-C}_4\text{H}_6)]^{2+}$ [3], $[\text{Ru}(\text{H}_2\text{O})_5(\eta^2\text{-C}_2\text{H}_4)]^{2+}$ [4], and *cis*- $[\text{Ru}(\text{H}_2\text{O})_4(\eta^2\text{-C}_2\text{H}_4)_2]^{2+}$ [4]. The aqueous phase ring-opening metathesis polymerization (ROMP) of 7-oxabicyclo[2.2.1]hept-5-ene derivatives in the presence of hydrated RuCl_3 as catalyst proceeds via $[\text{Ru}(\text{H}_2\text{O})_5(\eta^2\text{-alkene})]^{2+}$, which can be generated directly from

$[\text{Ru}(\text{H}_2\text{O})_6]^{2+}$ [5]. Although it remains unclear how the presumed metal–carbene intermediate in this aqueous-phase catalysis is generated, the discovery led directly to the first generation of well-defined ROMP catalysts based on carbene complexes of the type $[\text{RuCl}_2(\text{=CHR})(\text{PR}'_3)_2]$ (R = alkyl, aryl, =CH-CH=CPh_2 ; R' = Ph, Cy) [6–8].

Taube [1] suggested that the uniqueness of Ru^{II} and Os^{II} lies in the stability of the spin-paired nd^6 configuration and the radial extension of the $d(\pi)$ -orbitals, which allows back-bonding to suitable acceptor orbitals on the ligand. Although these suggestions were made in the context of ‘classical’ coordination chemistry, they are equally valid in accounting for the stability of the numerous η^1 -carbon complexes and half-sandwich, pseudo-octahedral η^5 -cyclopentadienyl and η^6 -arene complexes of Ru^{II} and Os^{II} [9]. Another contributing factor may be that Ru^{II} and Os^{II} are far less prone to form dinuclear complexes containing metal–metal multiple bonds than the early transition elements Mo, W and Re in their lower oxidation states.

^{*} Corresponding author. Tel.: +61 2 6125 3639; fax: +61 2 6125 3216.

E-mail address: bennett@rsc.anu.edu.au (M.A. Bennett).

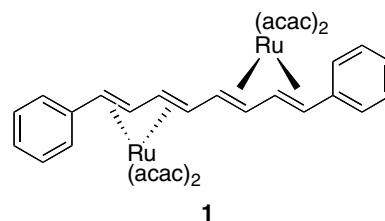
The presence of π -acceptor ligands in the coordination sphere of octahedrally coordinated ruthenium tends to stabilize the occupied metal π -orbitals (HOMO) and reduce the interelectronic repulsion in the metal ion, thus stabilizing Ru^{II} (t_{2g}^6) relative to Ru^{III} (t_{2g}^5). Thus, the reduction potentials $E_{1/2}$ of the $\text{Ru}^{\text{III}}/\text{Ru}^{\text{II}}$ couple for $[\text{Ru}(\text{NH}_3)_5(\eta^2\text{-alkene})]^{2+}$ complexes range from +0.83 V (alkene = propene) [10] to +0.98 V (alkene = styrene) [11], corresponding to a stabilization of the Ru^{II} level of ca. 0.75 V compared to $[\text{Ru}(\text{NH}_3)_6]^{2+}$ ($E_{1/2} = +0.05$ V vs. NHE) [12]. A similar trend is evident in the $E_{1/2}$ values (vs. NHE) for the aqua ions $[\text{Ru}(\text{H}_2\text{O})_6]^{2+}$ (+0.19 V) [13] and $[\text{Ru}(\text{H}_2\text{O})_5(\eta^2\text{-C}_2\text{H}_4)]^{2+}$ (+0.84 V) [14]. The electrogenerated one-electron oxidation products, $[\text{Ru}(\text{NH}_3)_5(\eta^2\text{-alkene})]^{3+}$ and $[\text{Ru}(\text{H}_2\text{O})_5(\eta^2\text{-alkene})]^{3+}$, have not been isolated or detected, because the alkene is probably weakly bound at the Ru^{III} level and is replaced rapidly by the solvent (usually water) in which the cyclic voltammetry is performed [10,11,15]. It is generally assumed that metal–ligand back-bonding is negligible at the Ru^{III} level, though the same may not be true for Os^{III} . Indeed, the alkyne–osmium(III) species $[\text{Os}(\text{NH}_3)_5(\eta^2\text{-PhC}_2\text{Ph})](\text{PF}_6)_3$ has been isolated by oxidation of $[\text{Os}(\text{NH}_3)_5(\eta^2\text{-PhC}_2\text{Ph})](\text{OTf})_2$ with $[\text{FeCp}_2]\text{PF}_6$ [16].

2. Reduction of $[\text{Ru}(\text{acac})_3]$: a route to $[\text{Ru}(\text{acac})_2\text{L}_2]$ complexes

In trying to design a system that might allow a comparison of the binding of unsaturated ligands at both Ru^{II} and Ru^{III} oxidation levels, we turned to acac^- as the co-ligand. The starting material, $[\text{Ru}(\text{acac})_3]$, is well defined and easily synthesized in high yield from hydrated RuCl_3 [17,18]. It undergoes an electrochemically reversible, metal-based one-electron reduction to the anion $[\text{Ru}(\text{acac})_3]^-$, whose negative $E_{1/2}$ value (typically ca. –0.70 V vs. Ag/AgCl , depending on solvent) reflects the effect of the three anionic ligands in stabilizing Ru^{III} relative to Ru^{II} [19–21]. The report of Sato et al. [22] in 1988 that heating $[\text{Ru}(\text{acac})_3]$ in 1:1 water–acetonitrile in the presence of zinc amalgam gave $[\text{Ru}(\text{acac})_2(\text{NCMe})_2]$ (isomeric configuration unspecified) in ca. 60% yield suggested a possible general procedure to synthesize a range of complexes of the $\text{Ru}(\text{acac})_2$ fragment. Later, Taube and co-workers [23] showed that

Sato's procedure affords the *cis*-isomer, whereas zinc amalgam reduction of $\text{trans-}[\text{RuCl}_2(\text{acac})_2]^-$ in acetonitrile at room temperature gives $\text{trans-}[\text{Ru}(\text{acac})_2(\text{NCMe})_2]$, which isomerizes on heating.

The reduction of $[\text{Ru}(\text{acac})_3]$ with zinc dust in ethanol in the presence of acyclic conjugated dienes, such as 2,4-hexadiene, 2,3-dimethylbutadiene, 2,4-dimethyl-1,3-pentadiene and 2-methylbutadiene, gives air-stable $\text{Ru}(\text{acac})_2$ complexes, isolated in ca. 60% yield, in which the transoid diene is coordinated in a η^2, η^2 mode [24,25]. Complexes of this type can exist in solution as a pair of diastereomers, as shown in Fig. 1 for the 2,4-hexadiene complex, which do not interconvert rapidly on the NMR time-scale at room temperature. Only small amounts of the corresponding *cis*-1,3-diene complexes can be detected in solution, although 1,3-cyclohexadiene retains its cisoid configuration in the similarly prepared complex $[\text{Ru}(\text{acac})_2(1,3\text{-C}_6\text{H}_8)]$. On reaction with $[\text{Ru}(\text{acac})_3]/\text{Zn}/\text{EtOH}$, 1,2,4,5-tetramethylcyclohexadiene forms a η^2, η^2 -complex similar to $[\text{Ru}(\text{acac})_2(\text{COD})]$ and $[\text{Ru}(\text{acac})_2(\text{NBD})]$, which can also be made similarly from $[\text{Ru}(\text{acac})_3]$ [26]. The reaction of 1,8-diphenyl-1,3,5,7-octatetraene with $[\text{Ru}(\text{acac})_3]/\text{Zn}/\text{EtOH}$ gives complex **1** in which two $\text{Ru}(\text{acac})_2$ fragments are coordinated in an *anti*-arrangement to the 1–4 and 5–8 transoid diene units [27].



We modified Sato's procedure by use of THF containing a few drops of water in place of acetonitrile, addition of the desired alkene, and heating the mixture for several hours. Either zinc amalgam or freshly activated zinc powder are suitable reducing agents. In this way, the cyclooctatetraene complex $[\text{Ru}(\text{acac})_2(\eta^2, \eta^2\text{-1,3,5,7-C}_8\text{H}_8)]$ has been obtained in good yield [28]. Cyclooctene gives the labile complex *cis*- $[\text{Ru}(\text{acac})_2(\eta^2\text{-}$

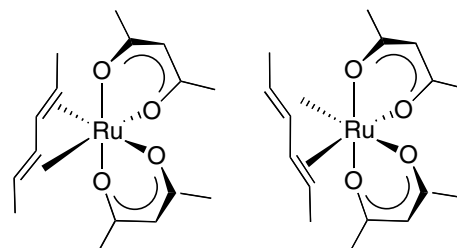


Fig. 1. Diastereomers of $[\text{Ru}(\text{acac})_2(\eta^2, \eta^2\text{-2,4-hexadiene})]$.

¹ Ligand abbreviations used in this paper: acac = acetylacetonate, 2,4-pentanedionato, $\text{C}_5\text{H}_7\text{O}_2$; 1,5-COD = 1,5-cyclooctadiene; NBD = norbornadiene, [2,2,1]bicyclohepta-2,5-diene; phen = 1,10-phenanthroline; dppe = 1,2-bis(diphenylphosphino)ethane; dppp = 1,3-bis(diphenylphosphino)propane; *S*-BINAP = *S*-2,2'-bis(diphenylphosphino)-1,1'-binaphthyl; OEP = dianion of 2,3,7,8,12,13,17,18-octaethylporphyrin; TPP = dianion of 5,10,15,20-tetraphenylporphyrin.

$C_8H_{14}_2$] (**2**), which is stable in solution only in the presence of an excess of cyclooctene [26], whereas the more stable ethene complex, *cis*-[Ru(acac)₂(η^2 -C₂H₄)₂] (**3**), can be isolated as a yellow-orange solid in ca. 60% yield [29]. At least for the mono-ene complexes, the presence of water in the THF seems to be beneficial, possibly because it increases the reducing power of the zinc and removes the by-product, Zn(acac)₂. The mono-ene complexes cannot be obtained by use of zinc in ethanol, because they decompose rapidly in contact with ethanol in the presence of air.

Similar procedures have been used to prepare *cis*-[Ru(acac)₂L₂] [2L = 2SbⁱPr₃, 2PⁱPr₃, (*S*)-BINAP] [30,31]; a few other examples of this class, including those having 2L = 2CO [32], 2PPh₃ [33–35], 1,5-COD [36], NBD [36] and phen [37], had been made previously by different methods.

Exceptionally, zinc reduction of [Ru(acac)₃] under CO does not give *cis*-[Ru(acac)₂(CO)₂] as the main product; the main species formed in aqueous THF under CO (1–2 bar) are the solvent complexes *trans*-[Ru(acac)₂(CO)(L)] (L = THF, H₂O), which show a strong ν (CO) band at ca. 1940 cm⁻¹ [38]. They are probably analogous to the complexes *trans*-[Ru(acac)₂(CO)(ROH)] (R = Me, Et, ⁱPr), which have been isolated by γ -irradiation of [Ru(acac)₃] in the appropriate alcohol; the structure of the methanol derivative has been determined by X-ray crystallography [39].

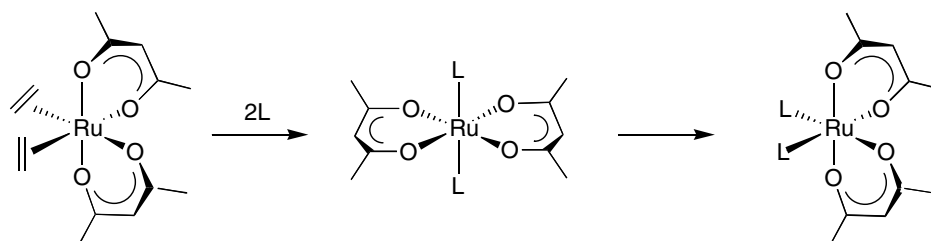
3. Chemistry of [Ru(acac)₂(η^2 -alkene)₂]

The *cis*-arrangement of the ethene molecules in [Ru(acac)₂(η^2 -alkene)₂] suggested by NMR spectroscopic data, and confirmed for the ethene complex **3** by single-crystal X-ray diffraction analysis [29], presumably maximizes back-bonding from Ru^{II}. In contrast to the related rhodium(I) complex [Rh(acac)(η^2 -C₂H₄)₂], however, the ethene molecules in the ruthenium(II) complex are mutually orthogonal, thus possibly reducing steric interference in the coordination sphere; in solution they are equivalent on the ¹H and ¹³C NMR time-scales,

even at -95 °C, indicative of rapid rotation. As expected for an octahedral d⁶ complex, intermolecular exchange with ethene is slow on the NMR time-scale, again in contrast with the behaviour of [Rh(acac)(η^2 -C₂H₄)₂].

The coordinated alkenes in **2** and **3** are readily replaced by a wide range of ligands under mild conditions, so that these complexes are convenient synthetic precursors. The stereochemical course of these octahedral substitution reactions can be followed in some detail. In most cases, the first product isolated from reactions with 2 mol. of ligand is *trans*-[Ru(acac)₂L₂], which on heating is transformed irreversibly into the *cis*-isomer (Scheme 1) [26]. For tertiary phosphines, this isomerization occurs most readily (at or below room temperature) for the bulky ligands PⁱPr₃ and PCy₃ [38], and least readily for PMe₃ (refluxing mesitylene) [26], which suggests that isomerization proceeds through initial dissociation of the tertiary phosphine via a fluxional, five-coordinate, probably square pyramidal intermediate Ru(acac)₂L. So great is the tendency to form a *trans*-isomer as the kinetic product of reaction that, with the bidentate ligands dppe and dppp, oligomeric intermediates [Ru(acac)₂(P-P)]_n can be isolated which are converted into the thermodynamically favoured *cis*-isomers only on heating in solution at ca. 140 °C [26].

Although the alkenes are undoubtedly displaced sequentially from **2** or **3**, there are only a few cases in which intermediates [Ru(acac)₂(η^2 -alkene)(L)] can be detected, apparently because most of the ligands listed in Scheme 1 displace the second alkene more rapidly than the first. Ammonia reacts with **3** at room temperature giving *trans*-[Ru(acac)₂(η^2 -C₂H₄)(NH₃)], which subsequently forms the *cis*-isomer, even at room temperature, while pyridine at room temperature gives a 3:2 mixture of *cis*- and *trans*-[Ru(acac)₂(η^2 -C₂H₄)(py)] which is converted into pure *cis*-isomer in refluxing benzene [29]. Under the same conditions, triphenylstibine reacts with either **2** or **3** to give complexes of the type *cis*-[Ru(acac)₂(η^2 -alkene)(SbPh₃)], which reacts further with Ph₃Sb to give *cis*-[Ru(acac)₂(SbPh₃)₂]; in neither step can a *trans*-isomer be detected. Werner et al. [30] have reported the preparation of the related complex



2 or 3

L = py, PPh₃, P(*p*-tol)₃, PMe₂Ph, PMePh₂, PMe₃, PEt₃, PⁱPr₃, PCy₃, P(OMe)₃, P(OPh)₃, AsPh₃, ^tBuNC

Scheme 1.

cis-[Ru(acac)₂(η²-C₂H₄)(SbⁱPr₃)] by reaction of *cis*-[Ru(acac)₂(SbⁱPr₃)₂] with ethene, but this type of ligand displacement does not occur for the less labile *cis*-[Ru(acac)₂(SbPh₃)₂].

Of the P-donor ligands listed in Scheme 1, triisopropylphosphine and tricyclohexylphosphine are unique in reacting in a 1:1 mol ratio with **3** in benzene to give isolable mono-substitution products *cis*-[Ru(acac)₂(η²-C₂H₄)(L)] [L = PⁱPr₃ (**4**), PCy₃ (**5**)], which then react further with L to give initially *trans*- and then *cis*-[Ru(acac)₂L₂] [40]. The ethene in complexes **4** and **5** is remarkably labile, being partly replaced even by THF, though there is no evidence from the Ru–C distances in the X-ray structures of the complexes that the Ru–C₂H₄ interaction is particularly weak. The species generated in THF possess unusually deshielded ³¹P NMR singlets (δ 87.3 for L = PⁱPr₃; δ 74.7 for L = PCy₃; values quoted relative to 85% H₃PO₄), and are believed to be either five-coordinate [Ru(acac)₂L] or its six-coordinate THF adduct. Species of the type [Ru(acac)₂(η²-alkene)] and [Ru(acac)₂(L)] are likely intermediates in the sequential replacement of alkene from **2** or **3**.

The coordinated ethene of complex **4** is also displaced reversibly by dinitrogen to give a binuclear complex containing bridging dinitrogen. [{Ru(acac)₂(PⁱPr₃)₂}(μ-N₂)] (**5**) (Scheme 2) [40]. This exists as a mixture of diastereomers **5a** and **5b** in solution arising from the presence of two chiral *cis*-[Ru(acac)₂L] fragments, although only the homochiral diastereomer **5a** is found in the solid state. It appears to crystallize preferentially and transforms slowly over time in solution to an equilibrium mixture (ca. 3:2) of **5a** and **5b**, possibly via an undetected mononuclear intermediate [Ru(acac)₂(η¹-N₂)(PⁱPr₃)]. The affinity of the [Ru(acac)₂(PⁱPr₃)] fragment for dinitrogen is so high that complex **4** scavenges dinitrogen from industrial grade dihydrogen that contains ca. 100 ppm dinitrogen. Ever since the discovery of [Ru(NH₃)₅N₂]²⁺ [41], ruthenium(II) has been notable for the large number of dinitrogen complexes that it forms and for the variety of co-ligands that may be present in the coordination sphere [42,43]. Apart from [Ru(H₂O)₅N₂]²⁺ and

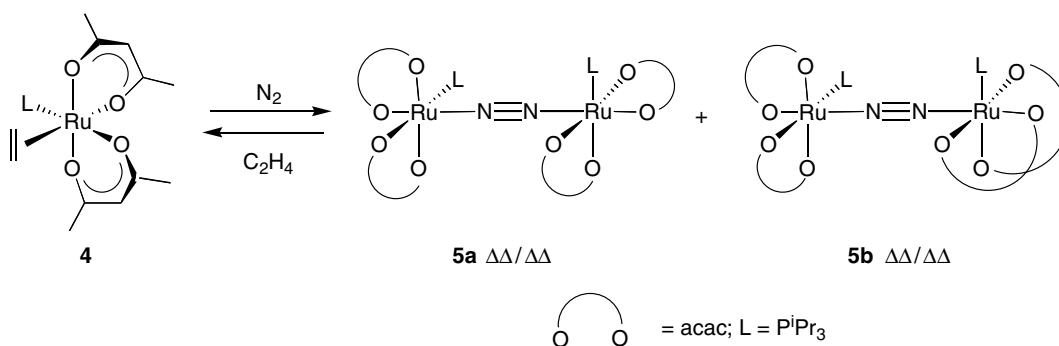
[{Ru(H₂O)₅}(μ-N₂)]⁴⁺ [44,45], however, complex **5** is the only example of a well-characterized ruthenium(II)–dinitrogen complex having an O-donor in the coordination sphere.

Vinylidene complexes [Ru(acac)₂(=C=CPhR)(L)] (R = H, SiMe₃) have been obtained by reaction either of *cis*-[Ru(acac)₂L₂] or the ethene complexes *cis*-[Ru(acac)₂(η²-C₂H₄)(L)] (L = PⁱPr₃, SbⁱPr₃) with PhC≡CH, Me₃SiC≡CH or PhC≡CSiMe₃, and allenylidene complexes *cis*-[Ru(acac)₂(=C=C=CPh₂)(L)] have been prepared similarly by use of HC≡C–CPh₂(OAc) [30]. Attempts to detect the presumed intermediate η²-alkyne complexes have been unsuccessful.

4. Redox behaviour

With the exception of *cis*-[Ru(acac)₂(CO)₂], all the [Ru(acac)₂L₂] complexes undergo reversible or nearly reversible one-electron oxidation by cyclic voltammetry (CV) at –50 °C. Selected values of half-wave potentials *E*_{1/2} (Ru^{III}/Ru^{II}) vs. Ag/AgCl for [Ru(acac)₂L₂] and [Ru(acac)₂(L)(L')], taken from our own work and from that of Heath's group [21], are listed in Table 1. The values range from –0.65 V for [Ru(acac)₃][–] to +0.95 V for *cis*-[Ru(acac)₂(η²-C₂H₄)₂] (**3**), corresponding, as a broad approximation, to the expected stabilization of the Ru^{II} level by stronger π-acceptor ligands. Thus, ligands such as CO and ^tBuNC cause large shifts to positive potentials, whereas O- and N-donor ligands give rise to more negative potentials; tertiary phosphines and phosphites are intermediate. Alkenes such as 1,5-COD and ethene strongly favour Ru^{II}, though not as strongly as CO, in accord with expectations based on their relative π-acceptor abilities. Of the alkene complexes examined, those containing ethene are less easily oxidized than those containing cyclooctene, presumably as a consequence of the electron-donating alkyl substituents in the latter.

Another trend evident from Table 1 is that *trans*-isomers are always more easily oxidized than their *cis*-counterparts, the difference in *E*_{1/2}-values being greater



Scheme 2.

Table 1
 $E_{1/2}$ (Ru^{III}/Ru^{II}) values for selected [Ru(acac)₂(L)(L')] complexes^a

L, L'	<i>cis</i>	<i>trans</i>	Ref.
NMe ₃ , NMe ₃		−0.20	[21b]
py, py	+0.01	−0.04	[21a]
MeCN, MeCN	+0.24	+0.12	[21b]
PMe ₃ , PMe ₃	+0.26	+0.00	[21b]
P ⁱ Pr ₃ , P ⁱ Pr ₃	+0.02	−0.14	[40]
PPh ₃ , PPh ₃	+0.37	+0.07	[21a]
AsPh ₃ , AsPh ₃	+0.34	+0.15	[21b]
SbPh ₃ , SbPh ₃	+0.39		[21b]
P(OMe) ₃ , P(OMe) ₃	+0.70	+0.22	[21b]
^t BuNC, ^t BuNC	+0.74	+0.25	[21b]
CO, CO	+1.65 ^b		[21a]
CO, PCy ₃	+0.92	+0.64	[40]
CO, PPh ₃	+1.10	+0.76	[21b]
C ₈ H ₁₄ , C ₈ H ₁₄	+0.77		[21a]
C ₂ H ₄ , C ₂ H ₄	+0.95		[29]
C ₈ H ₁₄ , NH ₃	+0.23		[21b]
C ₂ H ₄ , NH ₃	+0.37	+0.37	[29]
C ₂ H ₄ , P ⁱ Pr ₃	+0.42		[40]
C ₂ H ₄ , PCy ₃	+0.43		[40]
C ₈ H ₁₄ , MeCN	+0.44		[21b]
C ₈ H ₁₄ , SbPh ₃	+0.44		[21b]
C ₂ H ₄ , MeCN	+0.56		[29]
C ₂ H ₄ , SbPh ₃	+0.59		[29]

^a Volts vs. Ag/AgCl/CH₂Cl₂, 0.45 M [^tBu₄N]PF₆, 0.05 M [^tBu₄N]Cl; $E_{1/2}$ (Fe^{III}/Fe^{II}) for ferrocene = +0.55 V.

^b Irreversible process.

for the more strongly π -acceptor ligands, i.e., ca. 0.5 V for P(OMe)₃ and ^tBuNC, ca. 0.3 V for tertiary phosphines, ca. 0.1 V for CH₃CN, and 0.05 V for pyridine. This trend is explicable on the assumption first made by Bond and co-workers [46] in their study of Group 6 dicarbonyls M(CO)₂(dppe)₂, and later extended by Bursten and co-workers [47–49], that the HOMO of the *cis*-isomer from which the electron is removed is stabilized by interaction with the more strongly π -acceptor ligands.

Many of the ruthenium(III) complexes [Ru(acac)₂L₂]⁺ having $E_{1/2}$ values of less than ca. 0.4 V (e.g., those containing py, CH₃CN and tertiary phosphines) can be isolated by treatment of [Ru(acac)₂L₂] with one-electron oxidants such as [FeCp₂]⁺ or Ag⁺. In contrast with the M(CO)₂(dppe)₂ system, there is no interconversion of isomers during the redox process. Although their potentials are too high to permit isolation of salts, the alkene–ruthenium(III) cations can be electrogenerated in an optically transparent thin layer electrode (OTTLE) cell, detected by their characteristic electronic spectra, and maintained in CH₂Cl₂ solution for long periods at −50 °C. For example, the bands in the electronic spectrum of *cis*-[Ru(acac)₂(η^2 -C₂H₄)₂] (3) at 32,700 cm^{−1} (ϵ 6000 M^{−1} cm^{−1}) and 38,800 cm^{−1} (ϵ 8000 M^{−1} cm^{−1}) are replaced, on electro-oxidation at −50 °C with an applied potential of +1.20 V (vs. Ag/AgCl), by bands at 13,300 cm^{−1} (ϵ 2100 M^{−1} cm^{−1}), 16,900 cm^{−1} (ϵ 1200 M^{−1} cm^{−1}), and 34,100 cm^{−1}

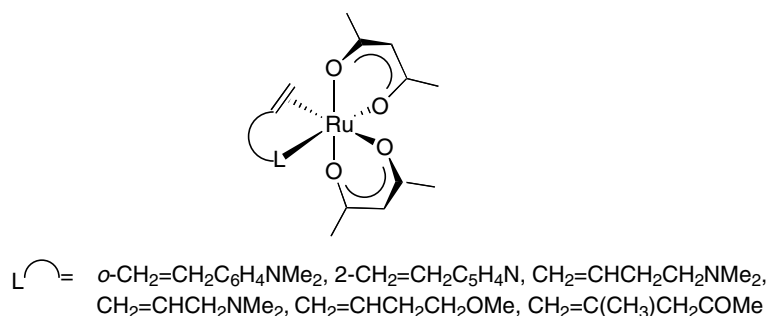
(ϵ 8000 M^{−1} cm^{−1}) due to the one-electron oxidation product [29]. The original spectrum is regenerated by application of a potential of +0.70 V and the observation of isosbestic points during both oxidation and reduction confirms the presence of just two absorbing species in solution. Similar observations have been made for [Ru(acac)₂(1,5-COD)] [21] and for the series [Ru(acac)₂(η^2 -alkene)(L)] (L = MeCN, SbPh₃, NH₃) [29]: the bands at ca. 25,000 cm^{−1} in the latter compounds are replaced on electro-oxidation by a band or pair of bands in the range 13,000–17,000 cm^{−1}. Generally, the one-electron oxidation products are not stable at room temperature, as shown by the irreversible changes in their electronic spectra. Deep blue solutions of the presumed ruthenium(III)–alkene complex are generated by treatment of *trans*-[Ru(acac)₂(η^2 -C₂H₄)(NH₃)] with AgPF₆ at −70 °C, but these decompose rapidly at room temperature, and slowly even at −20 °C. Similar treatment of *cis*-[Ru(acac)₂(η^2 -C₈H₁₄)(SbPh₃)] gives a deep blue solid, which appears to be stable at room temperature and, according to evidence from ESR spectroscopy, electrochemical behaviour, and electronic spectroscopy, is the ruthenium(III)–alkene salt *cis*-[Ru(acac)₂(η^2 -C₈H₁₄)(SbPh₃)]PF₆.

This observation suggests that a wider range of stable ruthenium(III)–alkene cationic complexes might be accessible if tertiary stibines [50] were present as co-ligands. The stability of such salts might also be increased by use of larger, less nucleophilic anions, such as [B(C₆F₅)₄][−]; for example, the long-lived, one-electron oxidation product of [Cr(CO)₃(η^6 -C₆H₆)] can be generated in CH₂Cl₂/[^tBu₄N][B(C₆F₅)₄] [51].

5. Chelate mono-alkene complexes of Ru(acac)₂

One approach to the stabilization of ruthenium(III)–alkene coordination is to employ mono-alkenes that also contain N- and O-donor centres. While the alkene in these potentially chelate ligands will favour ruthenium(II), the N- and O-donors can be expected to shift the $E_{1/2}$ values in favour of the higher oxidation state. Ligands of this type include 2-vinyl-*N,N*-dimethylaniline, *o*-CH₂=CH-C₆H₄NMe₂, 2-allylpyridine 2-CH₂=CHCH₂C₅H₄N, but-3-enyldimethylamine, CH₂=CHCH₂CH₂NMe₂, but-3-enylmethyl ether, CH₂=CHCH₂CH₂OMe, and mesityl oxide, CH₂=C(CH₃)CH₂COCH₃ (Fig. 2), whose Ru^{II}(acac)₂ complexes are best prepared by the usual Ru(acac)₃/Zn procedure [52].

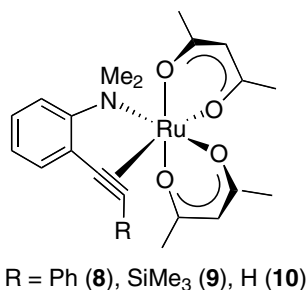
Like [Ru(acac)₂(η^2 , η^2 -2,4-hexadiene)] (see above), these complexes exist as a pair of diastereomers, distinguishable by ¹H and ¹³C NMR spectroscopy, which arise from the chirality of the *cis*-[Ru(acac)₂] fragment and of the coordinated mono-substituted alkene (Fig. 3). Each diastereomer contains a pair of enantiomers, *R* Δ /*S* Δ and *R* Λ /*S* Λ . The diastereomers of the

Fig. 2. Ru(acac)₂ complexes of chelate monoalkenes.

N-donor complexes are formed in about equal amounts under typical reaction conditions and do not interconvert rapidly at room temperature or on column chromatography, but prolonged heating in vacuo or in refluxing toluene finally gives a thermodynamic ratio of ca. 1:9 for the *RA*/*SA*, *RA*/*SA* pair. In the complexes of the O-donors this ratio is established even in the first isolated reaction products, perhaps because the greater lability of the Ru–O bond allows more readily interconversion of the diastereomers.

The complexes undergo reversible electrochemical one-electron oxidation with $E_{1/2}$ values in the range 0.3–0.6 V vs. Ag/AgCl, as shown in Table 2. The $E_{1/2}$ values for each diastereomer differ by ca. 100 mV, the kinetic isomers *RA*/*SA* being more easily oxidized than the *RA*/*SA*. Thus, cyclic voltammetry provides an independent means of estimating diastereomeric ratios. Moreover, the difference in $E_{1/2}$ values for the diastereomers is sufficient to enable a separation by differential chemical oxidation. Thus, if an approximately 1:1 mixture of the diastereomers of [Ru(acac)₂(*o*-CH₂=CHC₆H₄-NMe₂)] (**6**) is treated with 0.5 equiv. AgPF₆, the *RA*/*SA* diastereomer is almost completely converted into the deep blue ruthenium(III) salt [6]⁺ · PF₆⁻, leaving the *RA*/*SA* diastereomer unchanged.

The ruthenium(III) complexes of the chelate monoalkene ligands are deep blue, air-stable solids. Their ESR and electronic spectra resemble those of typical Ru^{III} complexes, hence a description of these compounds as Ru^{II} complexes of a ligand cation radical

Fig. 3. Ru(acac)₂ complexes of chelate monoalkynes.Table 2
 $E_{1/2}$ (Ru^{III}/Ru^{II}) values for *cis*-[Ru(acac)₂] chelate complexes

Ligand	$E_{1/2}$ ^a	Ref.
<i>o</i> -CH ₂ =CHC ₆ H ₄ NMe ₂ (6)	+0.42, +0.52 ^b	[52]
2-CH ₂ =CHCH ₂ C ₅ H ₄ N	+0.38, +0.47 ^b	[52]
CH ₂ =CHCH ₂ CH ₂ NMe ₂	+0.32, +0.44 ^b	[52]
CH ₂ =CHCH ₂ NMe ₂ (7)	+0.28, +0.42 ^b	[54]
CH ₂ =C(Me)CH ₂ COMe	+0.44, +0.52 ^b	[54]
CH ₂ =CHCH ₂ CH ₂ OMe	+0.43, +0.53 ^b	[54]
<i>o</i> -CH ₂ =CHC ₆ H ₄ PPh ₂	+0.67, +0.67 ^b	[21]
CH ₂ =CHCH ₂ CH ₂ PPh ₂	+0.54, +0.54 ^b	[52]
CH ₂ =CHCH ₂ CH ₂ PMe ₂	+0.46, +0.46 ^b	[52]
<i>o</i> -Me ₃ SiC≡CC ₆ H ₄ NMe ₂ (9)	+0.19	[56]
<i>o</i> -PhC≡CC ₆ H ₄ NMe ₂ (8)	+0.26	[56]
<i>o</i> -HC≡CC ₆ H ₄ NMe ₂ (10)	+0.27	[56]
<i>o</i> -Me ₂ NC ₆ H ₄ CH=C ^c	+0.46 ^d	[52]
<i>o</i> -Me ₂ NC ₆ H ₄ CO (13)	-0.55	[52]
<i>o</i> -Me ₂ NC ₆ H ₄ C=C(Ph)(py) (14)	-0.50	[65]
<i>o</i> -Me ₂ NC ₆ H ₄ COCH ₂ Ph (16)	+0.05	[65]
<i>o</i> -Me ₂ NC ₆ H ₄ COCH(PPh ₃) (18)	-0.45	[65]

^a Volts vs. Ag/AgCl/CH₂Cl₂, 0.45 M [ⁿBu₄N]PF₆, 0.05 M [ⁿBu₄N]Cl; $E_{1/2}$ (Fe^{III}/Fe^{II}) for ferrocene = +0.55 V.

^b Values for two diastereomers.

^c Dinuclear complex (see text).

^d Value for Ru^{II,II} to Ru^{III,II} process.

is not valid. Comparison of the X-ray structures of both diastereomers of **6** with that of the *RA* diastereomer of [6]⁺ · SbF₆⁻ demonstrates that the alkene is more weakly bound at the ruthenium(III) level. In particular, the Ru–C(alkene) distances increase on oxidation from ca. 2.15 to 2.24 Å; correspondingly, there is a less pronounced decrease in the C=C distance from ca. 1.38 to 1.35 Å. This trend is as expected on the basis of the Dewar–Chatt–Duncanson model of metal–alkene bonding, since the electron removed on oxidation occupies a HOMO arising from overlap of a filled metal orbital (t_{2g} in a regular octahedron) with an alkene π^* -orbital [53].

As expected, the isolated ruthenium(III) complexes undergo electrochemical reduction to their ruthenium(II) precursors, the $E_{1/2}$ values being the same as those observed for the Ru^{II} → Ru^{III} process. However, the relative intensities of the waves due to the diastereomers are different from those observed in the oxidation,

that due to the $R\Delta/S\Delta$ isomer now being relatively more intense than that due to $R\Lambda/S\Lambda$. At the Ru^{III} level, the $R\Lambda/S\Lambda$ diastereomer of 6^+ isomerizes over a period of hours at room temperature to the $R\Delta/S\Delta$ diastereomer, the final thermodynamic ratio of $R\Delta/S\Delta$ to $R\Lambda/S\Lambda$ being ca. 9:1. The greater lability at the Ru^{III} level is probably a consequence of facile reversible dissociation of the weakly bound alkene end of the bidentate ligand. The factors that are responsible for this remarkable reversal of preference in enantioface coordination of the alkene between the two oxidation states remain unclear. It is interesting that a similar difference in orientation is observed in the $\text{Mo}^{\text{II}}/\text{Mo}^{\text{III}}$ couple $[\text{Mo}(\eta^5\text{-C}_5\text{H}_5)(\eta^3\text{-C}_3\text{H}_5)(\eta^4\text{-C}_4\text{H}_6)]^{n+}$ ($n = 0, 1$), the allyl group being in the “prone” position for $n = 0$ and “supine” for $n = 1$ [54].

Even allyldimethylamine, $\text{CH}_2=\text{CHCH}_2\text{NMe}_2$, forms a chelate $\text{Ru}(\text{acac})_2$ complex (**7**), despite the presence of only one carbon atom between the donor centres [55]. The isolated complex has the $R\Lambda/S\Delta$ configuration which is also thermodynamically favoured for **6**. It predominates (ca. 90%) even in the product obtained directly from the usual $\text{Ru}(\text{acac})_3/\text{Zn}$ preparation, although the minor diastereomer is detectable in the NMR spectra and cyclic voltammograms. The greater lability of **7** is probably associated with the relatively weak and asymmetric coordination of the alkene unit: the $\text{C}=\text{C}$ bond length [1.321(5) Å] is close to that in free ethene and the $\text{Ru}-\text{C}(\text{alkene})$ distances differ significantly [2.165(3) and 2.118(3) Å to the outer and inner carbon atoms, respectively]. In contrast with the electrochemical behaviour of the $6/6^+$ couple, the contours of the AC voltammograms of $7/7^+$ depend on both scan rate and temperature and can be explained qualitatively on the basis of the greater lability of coordinated allyldimethylamine [55].

The *cis*- $[\text{Ru}(\text{acac})_2]$ complexes of the alkene-tertiary phosphines *o*- $\text{CH}_2=\text{CHC}_6\text{H}_4\text{PPh}_2$ and $\text{CH}_2=\text{CHCH}_2\text{-CH}_2\text{PR}_2$ ($\text{R} = \text{Ph, Me}$) also undergo reversible oxidation by cyclic voltammetry to the corresponding Ru^{III} cations. Although diastereomers are clearly present in approximately equal amounts at the Ru^{II} level, as shown by NMR spectroscopy, their $E_{1/2}$ values are not distinguishable (Table 2), and we have been unable to separate the diastereomers by other methods [55].

6. Chelate alkyne, carbene, vinylidene and acyl complexes of $\text{Ru}(\text{acac})_2$

Although we have been unable to prepare alkyne analogues of $[\text{Ru}(\text{acac})_2(\eta^2\text{-C}_2\text{H}_4)_2]$ or $[\text{Ru}(\text{acac})_2(\eta^2\text{-C}_2\text{H}_4)(\text{L})]$, we have isolated some chelate mono-alkyne complexes (Fig. 3) by zinc reduction of $[\text{Ru}(\text{acac})_3]$ in the presence of the appropriate 2-ethynyl-*N,N*-dimethylaniline ligands [56].

These complexes undergo reversible, one-electron oxidation by cyclic voltammetry with $E_{1/2}$ values that are 150–250 mV less than those for the analogous alkene complexes (Table 2). Comparable differences between alkene and alkyne complexes have been observed in the $[\text{Ru}(\text{NH}_3)_5\text{L}]^{2+}$ series, e.g., for $\text{L} = \text{C}_2\text{H}_2$ and C_2H_4 , the $E_{1/2}$ values (vs. NHE) are +0.67 and +0.93 V, respectively [2]. The one-electron oxidation products of **8** and **9** have been isolated as deep blue solids from the reaction with $[\text{FeCp}_2]\text{PF}_6$. As for their alkene counterparts, their ESR and electronic spectra establish that they are best regarded as genuine ruthenium(III) complexes.

Comparison of the X-ray structure of $[\text{Ru}(\text{acac})_2(o\text{-PhC}\equiv\text{CC}_6\text{H}_4\text{NMe}_2)]$ (**8**) with that of $[\mathbf{8}]^+ \cdot \text{PF}_6^-$ indicates that, in contrast with the alkene analogues **6** and $[\mathbf{6}]^+ \cdot \text{SbF}_6^-$, the unsaturated fragment is somewhat more strongly bound to Ru^{III} than Ru^{II} . Thus, the $\text{Ru}-\text{C}(\text{alkyne})$ distances in $[\mathbf{8}]^+$ [2.080(3), 2.133(4) Å] are significantly less than those in **8** [2.113(5), 2.183(5) and 2.107(5), 2.172(5) Å for the two independent molecules in the unit cell]. Correspondingly, the $\text{C}\equiv\text{C}$ distance in $[\mathbf{8}]^+$ [1.245(4) Å] is slightly greater than that in **8** [1.224(6), 1.240(6) Å for the independent molecules], both being greater than that in the free ligand [1.190(3) Å]. These trends are also reflected in the IR $\nu(\text{C}\equiv\text{C})$ bands [ca. 1990, 1969 and 2218 cm^{-1} for **8**, $[\mathbf{8}]^+$, and the free ligand, respectively]. An even more marked trend in the same direction has been observed in the IR $\nu(\text{C}\equiv\text{C})$ bands of $[\text{Os}(\text{NH}_3)_5(\eta^2\text{-PhC}_2\text{Ph})]^{n+}$ [1910 cm^{-1} for $n = 2$, 1818 cm^{-1} for $n = 3$] [16]. In contrast, the $\nu(\text{C}\equiv\text{C})$ band in the trimethylsilyl-substituted compound **9** is ca. 20 cm^{-1} lower in frequency than that in $[\mathbf{9}]^+$; unfortunately, X-ray structures of this pair have not been determined.

At this stage, therefore, we can conclude only that the alkyne-binding affinities of the Ru^{II} and Ru^{III} fragments $[\text{Ru}(\text{acac})_2\text{NR}_3]^{0,1+}$ probably do not differ greatly. Certainly the lower $E_{1/2}$ values for the alkyne complexes compared with their alkene counterparts are consistent with a relative strengthening of the metal-alkyne bond in the higher oxidation state.

The difference in behaviour of alkenes and alkynes can be traced to the presence of the additional, orthogonal π_{\perp} orbital in the alkynes, which enhances their π -donor ability. This is particularly evident in the alkyne complexes of early transition elements where the alkyne can donate more than two electrons [57]. Connelly et al. [58,59] have suggested that the electron removed on one-electron oxidation of alkyne complexes comes from an antibonding M-alkyne HOMO derived by overlap of the orthogonal π_{\perp} orbital with one of the filled metal orbitals (t_{2g} in regular octahedral symmetry), thus accounting for the contraction (and, presumably, strengthening) of the metal-alkyne bond observed in the $3d^6/3d^5$ pair $[\text{Cr}(\text{CO})_2(\eta^2\text{-PhC}\equiv\text{CPh})(\eta^6\text{-C}_6\text{HMe}_5)]^{n+}$

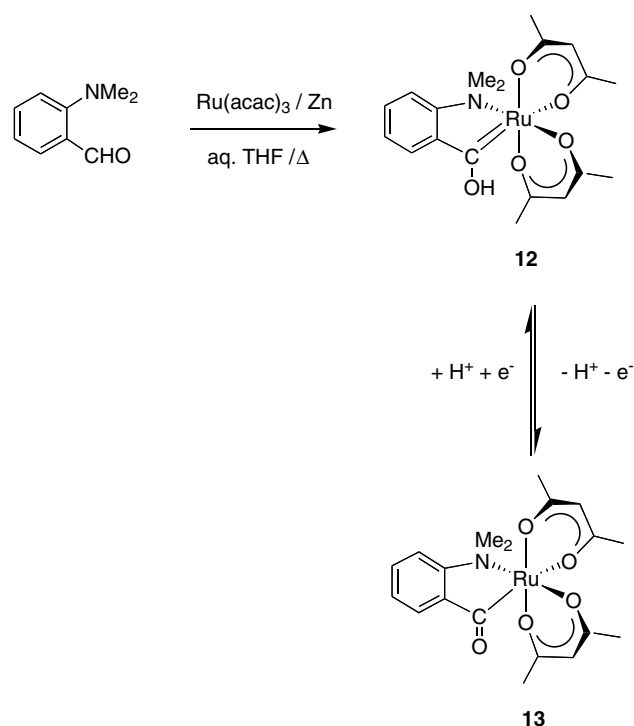
($n = 0, 1$) and the $4d^5/4d^4$ pair $[\text{Mo}(\text{CO})_2(\eta^2\text{-PhC}\equiv\text{CPh})(\text{Tp}')^{n+}]$ ($n = 0, 1$).

A deep violet vinylidene isomer (**11**) of $[\text{Ru}(\text{acac})_2(o\text{-HC}\equiv\text{CC}_6\text{H}_4\text{NMe}_2)]$ (**10**) is formed in small amounts in the preparation of the latter by the usual $[\text{Ru}(\text{acac})_3]/\text{Zn}$ procedure; it is more conveniently obtained by exposure of solutions of the crude trimethylsilyl-substituted compound **9** to air for 24 h [55]. Compound **11** itself contains two isomers, **11a** and **11b**, which can be separated by fractional crystallization from hexane. Both show dinuclear parent-ion peaks in their EI-mass spectra. Although X-ray structures have not been obtained, the presence of the $\text{Ru}=\text{C}=\text{CHR}$ unit is evident from the ^{13}C NMR spectra [δ 283.7 (C α), 112.9 (C β) (**11a**); 287.1 (C α), 114.0 (C β) (**11b**)] and from the presence of a diagnostic IR band at 1560 cm^{-1} . Since the $\text{Ru}=\text{C}=\text{CH}$ fragment must be linear, it is reasonable to formulate **11a** and **11b** as a pair of diastereomers in which the $\text{C}=\text{HC}_6\text{H}_4\text{NMe}_2$ -*o* unit bridges a pair of *cis*- $[\text{Ru}(\text{acac})_2]$ groups (Fig. 4). In CH_2Cl_2 both isomers show in the temperature range from -60 to $+20\text{ }^\circ\text{C}$ a reversible one-electron oxidation ($E_{1/2} +0.46\text{ V}$ vs. Ag/AgCl) and a second, irreversible process at about $+0.83\text{ V}$, which can be associated with successive $\text{Ru}^{\text{II,II}} \rightarrow \text{Ru}^{\text{II,III}}$ and $\text{Ru}^{\text{II,III}} \rightarrow \text{Ru}^{\text{III,III}}$ processes. These compounds would repay further investigation.

A diamagnetic, yellow-brown chelate hydroxycarbene complex of $\text{Ru}(\text{acac})_2$, $[\text{Ru}(\text{acac})_2\{\text{C}(\text{OH})\text{C}_6\text{H}_4\text{NMe}_2\text{-}o\}]$ (**12**), is obtained by zinc amalgam reduction of $[\text{Ru}(\text{acac})_3]$ in refluxing aqueous THF in the presence of 2-(dimethylamino)benzaldehyde. On exposure to air, solutions of **12** are rapidly oxidized to the paramagnetic acylruthenium(III) complex **13** [60] (Scheme 3); the process can be reversed by treatment of **13** with zinc amalgam in the presence of water. The acyl also undergoes reversible reduction in CH_2Cl_2 by cyclic voltammetry, the value of $E_{1/2}$, -0.55 V vs. Ag/AgCl , being only slightly less negative than that for $[\text{Ru}(\text{acac})_3]$. The first reduction product may be the ruthenium(II) acyl anion, **[13]**, which forms **12** either by protonation by traces of water or by hydrogen atom

abstraction from the $[\text{NEt}_4]\text{BF}_4$ used as supporting electrolyte. The latter behaviour has been observed in the anodic oxidation of the anionic benzoylchromium(0) complex $[\text{Cr}(\text{COPh})(\text{CO})_5]^-$ to give the phenylhydroxycarbenechromium(0) complex $[\text{Cr}\{\text{C}(\text{OH})\text{Ph}\}(\text{CO})_5]$ as the final product, formed via the radical $[\text{Cr}(\text{COPh})(\text{CO})_5]$ [61].

The generally similar X-ray structures of **12** and **13** show metrical differences that reflect the presence of hydroxycarbene and acyl groups. The $\text{Ru}-\text{C}(\text{acyl})$ bond in **13** [$1.956(6)\text{ \AA}$] is significantly longer than the $\text{Ru}=\text{C}(\text{hydroxycarbene})$ bond in **12** [$1.860(5)\text{ \AA}$], and the $\text{C}=\text{O}$ bond in **13** [$1.222(6)\text{ \AA}$] is significantly shorter than the $\text{C}-\text{OH}$ bond in **12** [$1.334(5)\text{ \AA}$]. The $\text{Ru}-\text{O}$ bond lengths *trans* to acyl in **13** [$2.180(4)\text{ \AA}$] and *trans* to



Scheme 3.

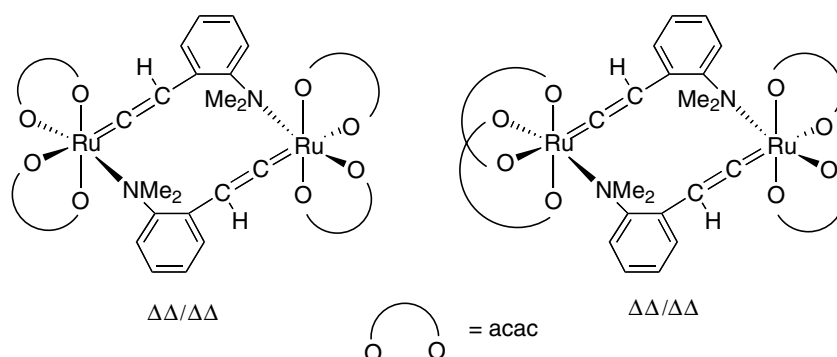


Fig. 4. Diastereomers of vinylidene complex **11**.

hydroxycarbene in **12** [2.187(3) Å] are both significantly greater than the other Ru–O bond lengths in both structures, which fall in the range 2.01–2.07 Å, thus indicating the high *trans*-influence of both acyl and hydroxycarbene ligands.

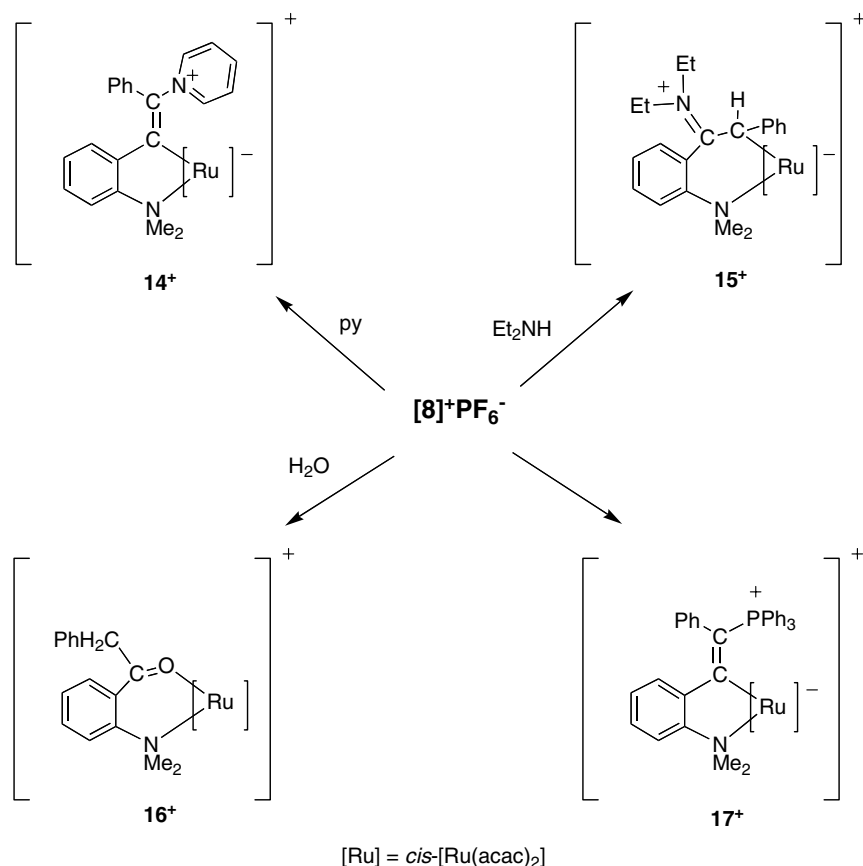
7. Reactivity of alkene and alkyne complexes of ruthenium(III)

The binding of unsaturated hydrocarbons to metal atoms in high oxidation states (i.e., having a formal positive charge or strongly electron-withdrawing co-ligands such as CO) is well known to render the hydrocarbons susceptible to nucleophilic attack, which usually occurs *exo* to the metal centre [62,63]. The addition of neutral or charged O- and N-nucleophiles to mono-alkenes, chelating alkenes, and dienes coordinated to Pd^{II}, Pt^{II} and Fe^{II} has been studied extensively and some of the reactions are important synthetically or industrially. Although this enhancement of reactivity has been attributed to the net withdrawal of electron density from the unsaturated carbon atoms, it has also been suggested on the basis of theoretical calculations that slippage from η^2 - to η^1 -coordination is required for external nucleophilic attack on an alkene [64].

We have made a preliminary survey of the reaction of nucleophiles with Ru^{III}-alkene and -alkyne complexes, focussing attention on the chelate N-donor complexes because of their stability at room temperature [65]. Despite the weak binding of the alkene function at the Ru^{III} level, neither it nor the alkyne are displaced by ligands such as CO, pyridine or PMe₃ from the chelate N-donor complexes of Ru^{II} or Ru^{III}. The most clear-cut examples of nucleophilic addition have been observed in the alkyne series (Scheme 4).

The addition of an excess of pyridine or dimethylamine to [Ru(acac)₂(*o*-PhC≡CC₆H₄NMe₂)]PF₆, [**8**]⁺ · PF₆⁻, gives dark red 1:1 adducts derived by nucleophilic addition to the alkyne. X-ray structural analysis shows that, in the pyridine adduct [**14**]⁺ · PF₆⁻, the nitrogen atom is attached to the β -carbon atom of the alkyne (i.e., one carbon atom removed from the *o*-Me₂NC₆H₄ fragment), thus generating a five-membered ring containing a Ru^{III}-C σ -bond [$d(\text{Ru}-\text{C})=2.031(7)$ Å] to carbon atom C α . In contrast, in the dimethylamine adduct [**15**]⁺ · PF₆⁻, the secondary nitrogen atom is attached via a double bond to the α -carbon atom and the hydrogen atom is on the β -carbon atom, thus giving a six-membered chelate ring [$d(\text{Ru}-\text{C})=2.194(3)$ Å].

Surprisingly, in [**14**]⁺ · PF₆⁻, the added pyridine is *endo* to the ruthenium atom, this stereochemistry being



Scheme 4.

opposite to that expected for external nucleophilic attack. One possible explanation is that pyridine first displaces the alkyne from the coordination sphere and that the alkyne then inserts into the metal-pyridine bond. It is also now recognized that the stereochemistry of the product isolated from the addition of a nucleophile to a coordinated alkyne need not necessarily define the mode of addition (see refs. [66,67] for examples).

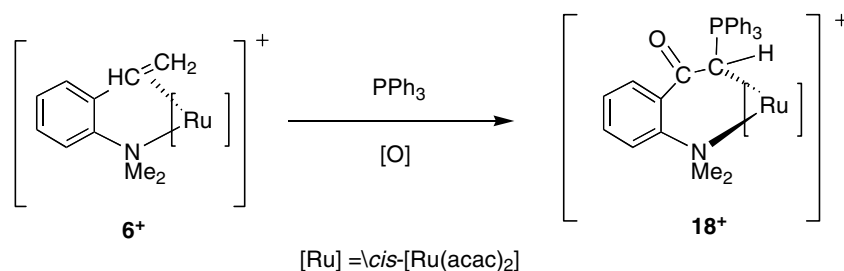
The product of nucleophilic addition of water to $[8]^+ \cdot PF_6^-$ is the chelate $\{(2\text{-dimethylamino})\text{phenyl}\}$ benzylketone complex $[16]^+ \cdot PF_6^-$. A possible intermediate is the tautomeric enol formed by *exo*-attack of water on the α -carbon atom. The red 1:1 adduct of $[8]^+ \cdot PF_6^-$ with methanol may be the vinyl ether corresponding to this tautomer but X-ray quality crystals could not be obtained. An iron (1-benzoyl)ethyl complex, $[CpFe(CO)\{P(OPh)_3\}\{CH(Me)COPh\}]$ has been obtained similarly by reaction of water with the but-2-yne complex $[CpFe(CO)\{P(OPh)_3\}(\eta^2\text{-MeC}\equiv\text{CMe})]^+BF_4^-$ in the presence of neutral alumina, and the corresponding vinyl ether complex has been obtained from the but-2-yne complex and methanol [68]. Water and methanol add to $[Os(NH_3)_5(\eta^2\text{-MeC}\equiv\text{CMe})(OTf)_2]$ to give the vinyl alcohol and vinyl ether complexes $[Os(NH_3)_5\{cis\text{-}\eta^2\text{-MeCH=C(OR)Me}\}](OTf)_2$ ($R = H, Me$), respectively; oxidation of the vinyl alcohol complex to the osmium(III) level forms the tautomeric 2-butanone complex [69], similar to the ruthenium(III) complex we have obtained.

The enamine complex $[15]^+ \cdot PF_6^-$ is probably formed similarly to $[16]^+ \cdot PF_6^-$ by attack of diethylamine on the α -carbon atom and subsequent proton transfer to the β -carbon atom. A 1:1 adduct of PPh_3 with $[8]^+ \cdot PF_6^-$ can also be isolated (Scheme 4); in frozen solution, like the other nucleophilic addition products, it shows a typical Ru^{III} ESR spectrum. We assume provisionally that the site of addition of PPh_3 in $[17]^+ \cdot PF_6^-$ is similar to that of pyridine in $[14]^+ \cdot PF_6^-$. The pyridine and water adducts show fully reversible Ru^{III}/Ru^{II} redox processes by cyclic voltammetry, with $E_{1/2}$ values of -0.50 and $+0.50$ V, respectively, vs. $Ag/AgCl$. The former value is much more negative than that for *trans*- $[Ru(acac)_2py_2]$ ($+0.01$ V) and this information provided an initial indication that pyridine had not added to the metal centre.

The reactions described above establish that the alkyne in *o*- $PhC\equiv CC_6H_4NMe_2$ is activated towards nucleophilic addition by coordination to the paramagnetic centre, ruthenium(III). Moreover, the products of reaction with pyridine, dimethylamine and PPh_3 are rare examples of complexes containing a $Ru^{III}\text{-C}$ σ -bond. The only previous examples are the five-coordinate σ -aryls containing porphyrinate ligands, $[Ru(Ar)(OEP)]$ [70] and $[Ru(Ar)(TPP)]$ [71], and cyclometallated octahedral complexes derived from substituted azobenzenes [72] and Schiff bases [73].

Attempts to carry out nucleophilic additions to the ruthenium(III) chelate alkene complex $[Ru(acac)_2(o\text{-CH}_2=CHC_6H_4NMe_2)]^+ \cdot PF_6^-$, $[6]^+ \cdot PF_6^-$, have been hindered by its facile reduction to the parent ruthenium(II) complex **6**. The red solid isolated from the addition of PPh_3 to $[6]^+ \cdot PF_6^-$ proved, unexpectedly, to be the triphenylphosphonium-ylide complex $[18]^+ \cdot PF_6^-$, as shown by X-ray crystallography (Scheme 5) [63]. The PPh_3 group is attached to the β -carbon atom in an *exo*-orientation relative to the metal atom, while the α -CH bond of the original vinyl group has been transformed into a keto group. Thus, nucleophilic attack of PPh_3 is accompanied by the loss of two hydrogen atoms and the gain of one oxygen atom. In contrast with the behaviour of the alkyne system (Scheme 4), the $Ru\text{-C}$ bond is formed to the same carbon atom ($C\beta$) as that to which the nucleophile has added, giving a six-membered chelate ring. The $Ru\text{-C}$ distance [2.160(4) Å] is similar to that to the β -carbon atom in the six-membered chelate ring of $[15]^+ \cdot PF_6^-$, while the $Ru\text{-C}\alpha$ distance of ca. 2.81 Å indicates that there is little or no interaction with carbon atom $C\alpha$. The $P\text{-C}\alpha$ distance [1.794(5) Å] is typical of P-ylide complexes that carry bulky substituents on the carbanion [74]. How the oxidation occurs, and whether the added oxygen atom is derived from air or water, are questions that remain to be answered.

Our preliminary results suggest that nucleophilic additions to alkene and alkyne complexes of ruthenium(III) would merit further investigation because they show different features from those of their more extensively studied platinum(II) and palladium(II) counterparts.



Scheme 5.

8. Conclusions

Fragments based on the unit $\text{Ru}^{\text{II}}(\text{acac})_2$ resemble $[\text{Ru}(\text{NH}_3)_5]^{2+}$ in their ability to bind unsaturated, π -acceptor ligands, as shown by the existence of stable compounds such as *cis*- $[\text{Ru}(\text{acac})_2(\eta^2\text{-C}_2\text{H}_4)_2]$, *cis*- or *trans*- $[\text{Ru}(\text{acac})_2(\eta^2\text{-C}_2\text{H}_4)(\text{L})]$ ($\text{L} = \text{NH}_3$, MeCN , P^iPr_3 , SbPh_3), $[\text{Ru}(\text{acac})_2(\text{P}^i\text{Pr}_3)(=\text{C}=\text{CHPh})]$, $[\{\text{Ru}(\text{acac})_2(\text{P}^i\text{Pr}_3)\}_2(\mu\text{-N}_2)]$, $[\text{Ru}(\text{acac})_2(o\text{-CH}_2=\text{CHC}_6\text{H}_4\text{NMe}_2)]$, and $[\text{Ru}(\text{acac})_2(o\text{-PhC}\equiv\text{CC}_6\text{H}_4\text{NMe}_2)]$. The presence of acac as an anionic, κ^2 -O-donor shifts redox potentials in favour of Ru^{III} and, by rendering the compounds soluble in the poorly coordinating solvent CH_2Cl_2 , allows the one-electron oxidation products to be either detected by spectroelectrochemistry or, in the case of ligands such as *o*- $\text{CH}_2=\text{CHC}_6\text{H}_4\text{NMe}_2$ and *o*- $\text{PhC}\equiv\text{CC}_6\text{H}_4\text{NMe}_2$, to be isolated. The limited evidence available indicates that the binding affinities of alkynes to Ru^{III} and Ru^{II} are comparable, whereas alkenes are more weakly bound to Ru^{III} than to Ru^{II} . Examples of the addition of uncharged nucleophiles to the chelate N-donor alkene and alkyne Ru^{III} -cations to give paramagnetic $\text{Ru}^{\text{III}}\text{-C}$ σ -bonded complexes have been demonstrated. The organometallic chemistry of ruthenium has long been dominated by complexes in which the metal is in 0, +2 and, to a lesser extent, +4 oxidation states [9]. It may be, however, that if the co-ligands are suitably chosen, paramagnetic Ru^{III} organometallic compounds, especially those containing η^1 -alkyl or η^1 -aryl groups, may become more common than previously suspected.

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